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Title: Fluid gel lubrication as a function of solvent quality

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Abstract

Soft tribology is of increasing interest in biotribology applications to approximate skin/skin and oral contact environments. As such a number of studies explore the tribological behaviour of food and consumer product/model systems have been reported. This work builds on this understanding by examining soft surface lubrication of Agar fluid gel as a function of solvent quality. Firstly with alcohols at varying concentrations and secondly with salts, using the well-known lyotropic effect, which from previous studies is known to affect the properties of gels.

Pure solvent systems showed patterns in friction reduction. Fluid gel lubrication behaviour was different when altering solvent quality and is suggested to be primarily an effect of changing gel structure, which is illustrated by approximate particle size distributions obtained for each sample. These effects can potentially be used to control food properties for enhanced behaviour in the mouth, or to better understand the structures that would form when using a fluid gel in more complex solvent containing products.

Keywords: Tribology, fluid gel, lubrication

Introduction

Tribology and lubrication behaviour is relevant for understanding perception of some sensory attributes during consumer assessment, either in the case of tongue palate interactions (de Wijk & Prinz, 2005; Malone, Appelqvist, & Norton, 2003) or for skin/skin interactions (Nakano, Kobayashi, Nakao, Tsuchiya, & Nagai, 2012). There is a constant drive to reformulate products to offer cheaper and more functional products. In many cases biopolymers are used to achieve this since they are often low cost and can have a relatively large impact on structure in low concentrations, however they do not always provide sufficient control over materials properties in simple forms (Renard, van de Velde, & Visschers, 2006). One extension of this application is the use of fluid gels, which are concentrated suspensions of gel particles in a continuous medium. These systems have been shown to provide a range of behaviours and functionalities by controlling processing conditions, allowing more tuneable material properties (D. A. Garrec & I.T. Norton, 2012; Norton, Frith, & Ablett, 2006).

Fluid gels are formed by applying shear to a biopolymer during its ordering process where it would otherwise form a large-scale gel network. The shear field serves to limit ordering to individual particles forming a concentrated gel suspension, the size and morphology of the particles is affected by a range of factors including the cooling rates and shear rate experienced offering a number of ways to manipulate behaviour (Norton, Jarvis, & Foster, 1999). There are two methods to creating a fluid gel within a solvent system other than water, the first is to create a fluid gel with pure water and add to the system in question, this allows for the fluid gel sample to be created with known properties. However, with this approach there will often be a dilution effect of the fluid gel sample reducing its packing fraction and therefore affecting its desirable rheological properties. Creating the fluid gel sample in the bulk product solvent can maintain the desirable gel properties but will complicate the formation process and potentially affect gel structure.

Ethanol and salts are common in a range of consumer products and food (salts more so) for a number of functional reasons, for example as solvents for other ingredients, preservatives and flavours. It is likely then that these would be present as solvents for a developed fluid gel system. As such, there were two main objectives of the work presented in this paper. Firstly, as the use of fluid gels in complex, solvent containing systems has not been previously investigated; we wanted to consider the effect of solvent quality on particle size. Secondly, we wanted to consider the lubrication behaviour of these fluid gel systems.

Materials and Methods

1.1 Materials

Methanol, ethanol and propanol were used to study the effect of alcohol; although methanol and propanol are not used in food/consumer products, ethanol is used widely from beverages to hand cream. Alcohols of different chain length were included to try to show if any contribution to lubrication is a function of the alcohol group itself or if the carbon chain influences lubrication (which is suggested in previous literature (Jahanmir, 1985)). Sodium chloride, trisodium citrate, sodium thiocyanate and trisodium phosphate were used to study the effect of anions through the lyotropic series. Again, although thiocyanate is not a food safe additative its inclusion in this study allows us to investigate the effects of anions on both side of the lyotropic series. All samples were supplied by Sigma Aldrich and used without further processing.

For the fluid gel systems agar powder (Sigma Aldrich) was used in conjunction with the relevant solvents as above. A list of produced samples is shown in Table 1. Phosphate was excluded since its very high pH (approximately pH 12) degraded the agar preventing a stable fluid gel from being produced(all other variations did not affect pH maintaining it around neutral.)

Table 1 Formulations used for fluid gel systems

Sample type (gel/solvent)	Agar concentration (% w/w)	Solvent concentration (mol fraction)
Agar/Ethanol	0.5	0, 0.02, 0.06, 0.08
Agar/Trisodium Citrate	0.5	0.002, 0.006, 0.01
Agar/Sodium Chloride	0.5	0.002, 0.006, 0.01
Agar/Sodium Thiocyanate	0.5	0.002, 0.006, 0.01

1.1 Methods

1.1.1 Fluid gel production

All fluid gel samples were produced by a similar method based on previous production methods by (Gabriele, Spyropoulos, & Norton, 2010), the base agar solution was produced by dissolving the desired weight of agar (and salts where applicable) into deionised water and raising the temperature to 90°C until dissolution was complete. The temperature was then lowered to 60°C to allow addition of alcohol (itself at 60°C) to avoid boiling and evaporation. These samples are then pumped through a scraped surface heat exchanger and pin stirred device in series. The flow rate of material was constant throughout at 25ml/min, the scraped surface heat exchanger was set at 60°C to control inlet temperature to the pin stirrer where structuring takes place, the pin stirrer was fixed at 5°C to produce gelation. Both units were operated at maximum rotational speed of 1400rpm.

1.1.2 Tribology measurements

Tribology measurements were carried out on all samples with the same method, using a mini traction machine (MTM, PCS instruments London). The equipment was configured with a steel ball and silicon elastomer disk as the contact surfaces. More details about the operation and configuration of the equipment can be found in (Garrec & Norton, 2011). The same ball was used for all tests whereas a fresh disk was used with each sample, cleaning of the surfaces was carried out between each sample by sonicating for 5 minutes in ethanol and 5 minutes in distilled water. Stribeck cures were produced in all cases by measuring friction force over a range of relative rotational speeds from 1 to 1000mm/s with a slide-roll-ratio of 50% and normal force of 2N. Six repetitions within the same sample alternating ascending and descending were carried out to detect hysteresis, three repetitions with fresh samples were averaged for final results. Error bars are presented as 1 standard deviation of the mean of all 18 measured curves per sample.

1.1.3 Surface tension measurements

Surface tension measurements of all samples were carried out using a K100 Tensiometer from Krüss GmbH, Hamburg (Germany). Measurements were made using a Wilhelmy plate method at 20°C and performed in triplicate. Error bars are presented as 1 standard deviation of the mean of the three repeats.

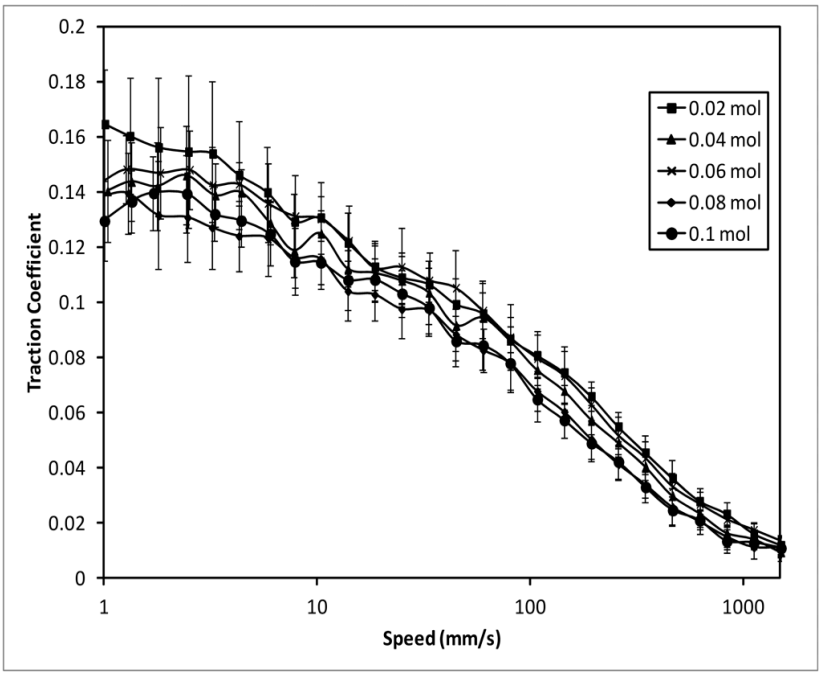
1.1.4 Mastersizer particle sizing measurements

All particle sizing was carried out using a Malvern mastersizer 2000 using a refractive index of 1.42 for agar particles, found from previous works with this system (Gabriele, et al., 2010). Average values for all particles are Sauter mean diameters (D3.2) which is the average diameter of a sphere with the same volume to surface area ratio of the measured particle. Graphs are average values of three samples, error bars were negligible and were omitted for clarity. However one standard deviation is given for average values as a guide. These measurements were the primary method to categorise the particle sizes created, since visualisation was not possible, due to the low polymer concentrations and closeness of refractive index between particle and water.

Results and discussion

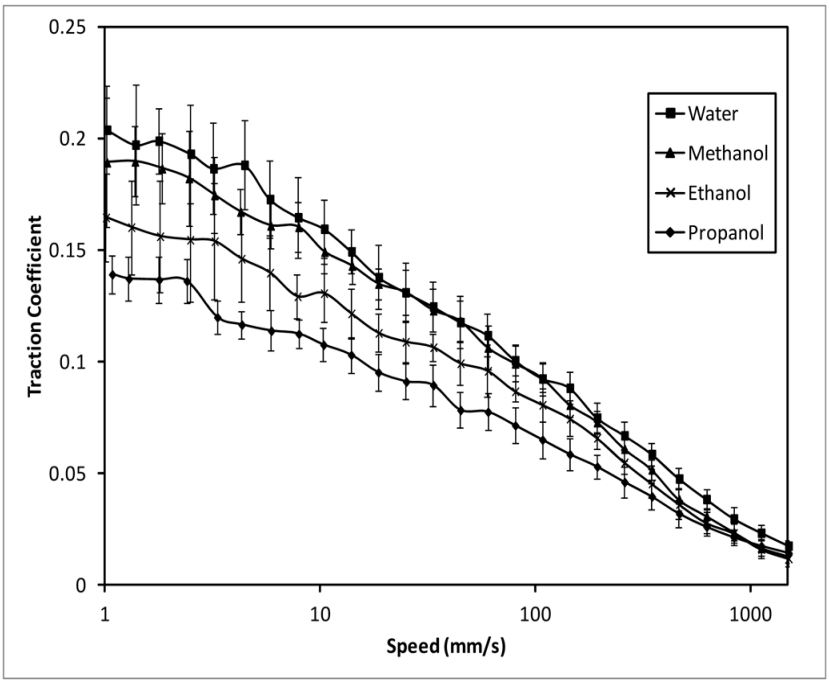
Initially data was obtained for the base solvent systems, Stribeck curves for methanol, ethanol and propanol were produced for a range of concentrations. Figure 1 shows an example of Stribeck curves for increasing ethanol concentration. For all of the pure solvent systems the characteristic shape of a Stribeck curve is present. Initially at low speed the highest friction is observed, it is here that surface contact dominates the friction experienced. With increasing speed entrainment occurs leading to a thin film of lubricant and some surface contact. Finally at significantly high speeds full surface separation is achieved leading to low frictions. While the Stribeck curves for increasing ethanol concentration show reduced friction over pure water lubrication, there is no discernable difference with concentration for the range studied.

Figure 1. Stribeck curves for ethanol concentrations



Examining the lubrication effects of the alcohol systems in comparison to deionised water we see there is a trend present in Figure 2, while methanol shows only slight reductions in friction over water there is a tendency to reduce friction with increasing chain length for ethanol and propanol. This reduction seems to be most evident at low speeds but continues through the mixed regime especially in the case of propanol. A mechanism is proposed in previous hard surface lubrication studies, where a close packed adsorbed monolayer forms, separating the surfaces and reducing friction (Jahanmir, 1985). In Jahanmir's work, high carbon value alcohols are shown to reduce friction with increasing chain length due to increased lateral cohesive forces between molecules in the adsorbed layer with increasing length. Jahanmir's study was, however, for metal surfaces in the boundary regime, and no soft tribology has been carried out for these systems. It is suggested that a similar situation must exist here and that once a lubricating layer has formed increasing concentration has no further effect. Surface tension measurements taken across the range of concentrations studied showed only small differences, in the case of ethanol surface tension decreased over the range from 45 to 38 mN/m, in contrast to this, values were more significantly different between alcohols. Surface tension for 0.08mol fraction of methanol, ethanol and propanol was 52, 39 and 28 mN/m respectively. It is expected that with reducing surface tension more material is retained between the surfaces creating greater lubrication, which is what is observed here.

Figure 2. Stribeck curves for alcohol systems at 0.01 mol fraction



Examining the salt effects we see a similar situation as alcohol systems, within salt concentrations there are no differences in the lubrication behaviour. There is however, a reduction in friction with the addition of salts over pure water, and there is a noticeable difference between types of anion. From Figure 3 we can see the reduction in friction is most noticeable in the boundary regime and initial mixed

regime although no differences are seen at the higher speeds. This helps to reinforce the suggestion that reductions in friction are from separating layers formed at the surface since at high speeds the bulk fluid achieves full surface separation. The effect is minimal for the thiocyanate samples, which are chaotropic according to the lyotropic series, but is clearer for the chloride, citrate and phosphate samples as you move further down the sequence. This trend is highlighted in Figure 4, with decreasing lyotropic number a reduction in friction is achieved for the low to intermediate speeds where surface contact is most dominant. Figure 5 shows surface tension data to the salt solutions, once again a decrease in tension is observed for most samples with the exception of chloride at the lower concentrations, in the same order as for the tribology results allowing a lubrication layer to form more readily.

Figure 3. Stribeck curves for salt systems

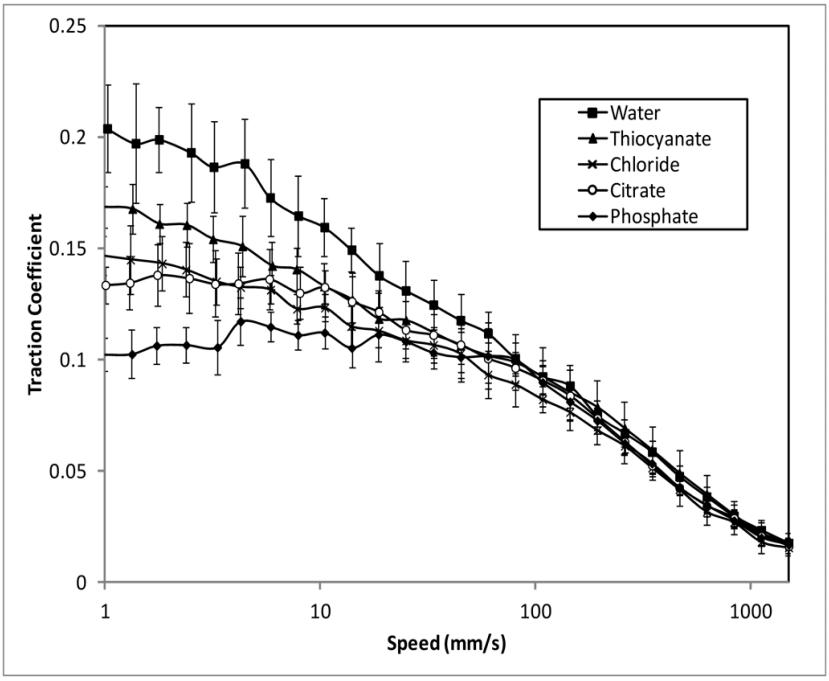


Figure 4. Traction coefficient by lyotropic number at fixed rotational speeds

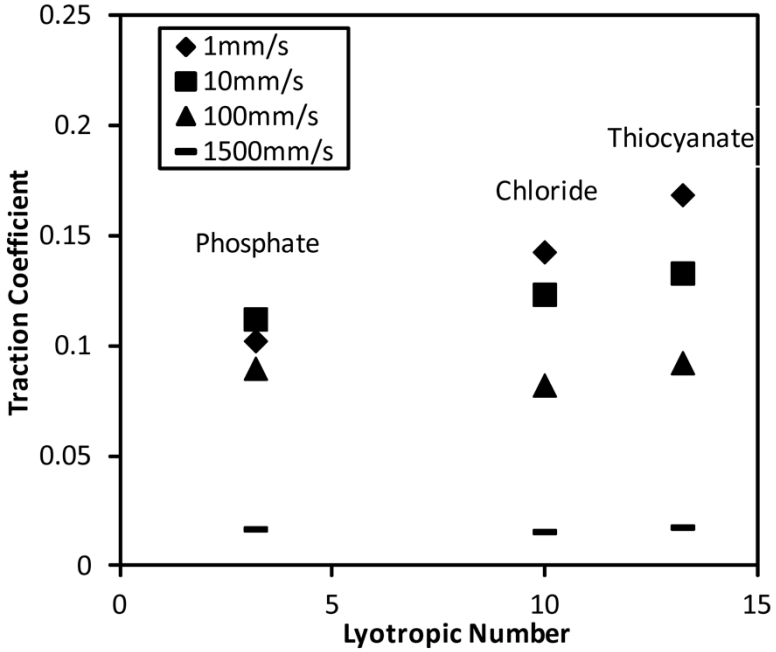
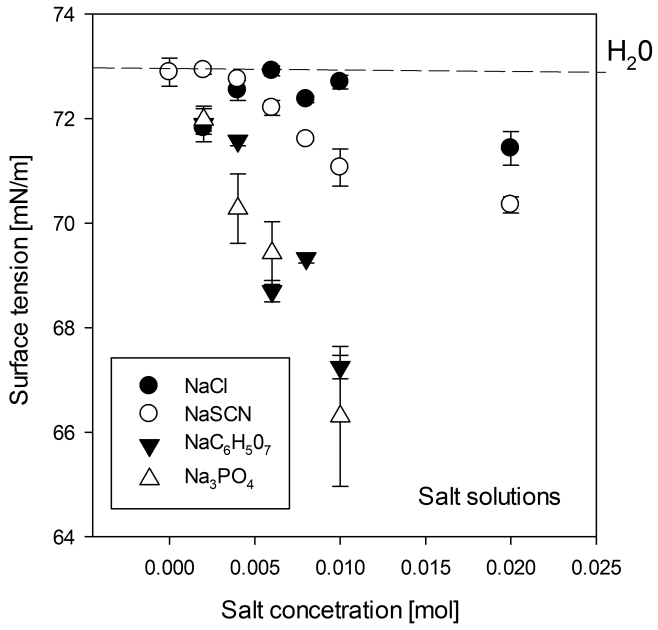


Figure 5. Surface tension of salt solutions



Combining these effects by measuring the response of ethanol/salt mixes produces similar results to measuring the salt systems since their effect is much greater than the ethanol alone, it is not clear however if there is a combined effect in reducing friction.

Moving to the gel system initially a baseline was formed with deionised water as the only solvent for the agar system. This Stribeck curve follows the form previously shown in (Gabriele, et al., 2010), the shape of a classic Stribeck curve is interrupted

by a second rise and fall in friction coefficient. The mechanism proposed here is due to the presence of particles in the bulk system. Initially the continuous medium and contact surfaces dictate friction since the gap size and roughness of the surfaces is much smaller than the particle sizes expected. As speed increases this gap widens reducing friction to a point where particles start to be entrained, this then causes a secondary rise in friction from a single particle layer contact environment. Once a critical level is reached a multilayer of particles starts to form decreasing friction once again until the hydrodynamic regime is reached and bulk material properties dictate lubrication behaviour. For the concentrations of ethanol considered here the same pattern is maintained with a secondary peak occurring at similar speeds for all concentrations. However for the higher concentrations an increase in friction is observed overall until approximately 200mm/s (Figure 6). This change in friction is suggested to be a result of the addition of ethanol changing particle sizes. Figure 7 shows distributions obtained by mastersizer measurements, the data for the 0.06 and 0.08 mol fraction samples show a broadening and shift to smaller sizes of the peak introducing a number of smaller particles which could fit between the contacting surfaces at lower speeds than the low concentration samples increasing the overall friction in this section. Previous work by (D. A. Garrec & I. T. Norton, 2012) do not see evidence of a double peak in Stribeck curves of carrageenan fluid gels since particle sizes are much smaller and so are assumed to entrain at lower speeds. It is also possible that at the higher concentrations of ethanol some precipitation of agar occurs, which could increase friction, although there was no evidence of this by observing pre gelled samples. Previous studies into agar gelation have shown that ethanol has a chaotropic effect, reducing its gelation temperature with increasing concentration and therefore affecting the structures formed (given that processing conditions are kept constant) (Hallsworth, Heim, & Timmis, 2003).

Figure 6. Stribeck curves for ethanol/agar systems

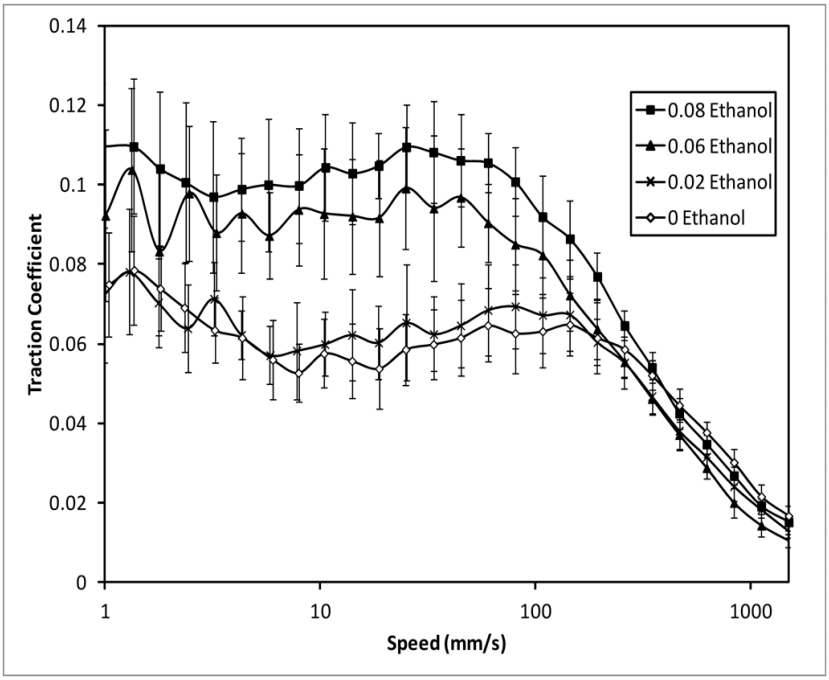
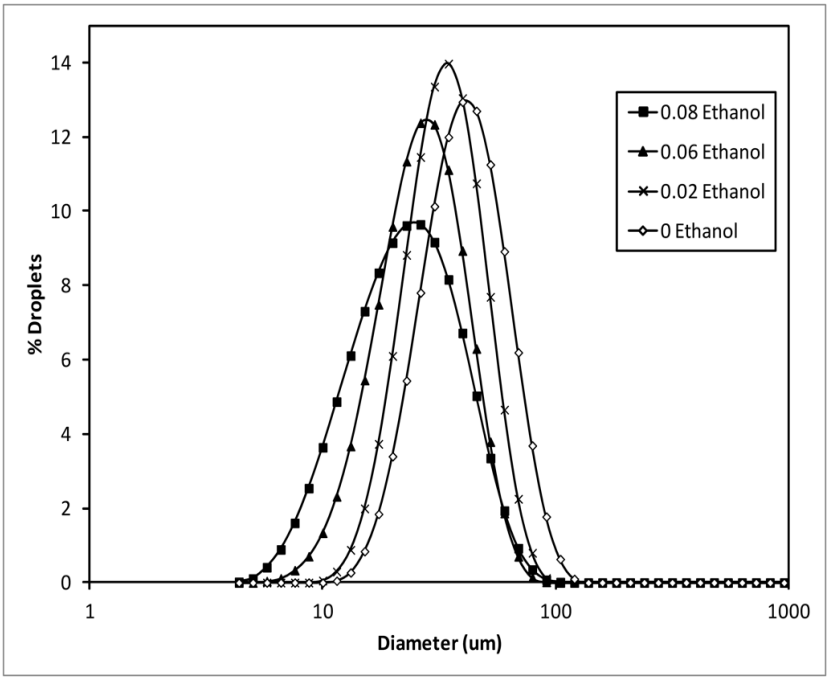


Figure 7. Particle size distributions for ethanol/agar systems



The effects of salt on gelation properties of agar have been previously studied in a number of different publications. It is known that chaotropic anions hinder the gelation of agar and supress its gelation temperature (Phillips & Williams, 2000) and that kosmotropic anions have the opposite effects (Piculell & Nilsson, 1989). The exact mechanism for this is not clear, but lyotropic effects are suggested to be a result of modifying solvent quality, or preferential adsorption of anion over water molecules to the agar structure (Piculell & Nilsson, 1989). It is assumed then that citrate being kosmotropic will have a strong stabilising effect on gelation, chloride will have a small stabilising effect and thiocyanate a strong destabilising effect, in all cases the cooling temperature at 5°C should be sufficient to induce gelation. First examining chloride in Figure 8 as a relatively neutral anion the characteristic fluid gel shape has been altered, a double peak is no longer evident. One possible explanation for the initial difference is that a large shift in particle sizes is observed compared to the ethanol samples moving the distributions from an average particle size (D3.2) of 35μm (± 0.35) to 90μm (± 0.93) but maintaining overall shape (Figure 9). This could prevent the initial formation of a monolayer of particles but instead, relying on the continuous phase for lubrication that has been shown here to reduce friction over pure water. These larger particles are likely a result of the promotion of gelation experienced forming slightly faster and softer gels than the control sample which the shear field does not limit to the same extent.

Figure 8. Stribeck curve for agar/chloride

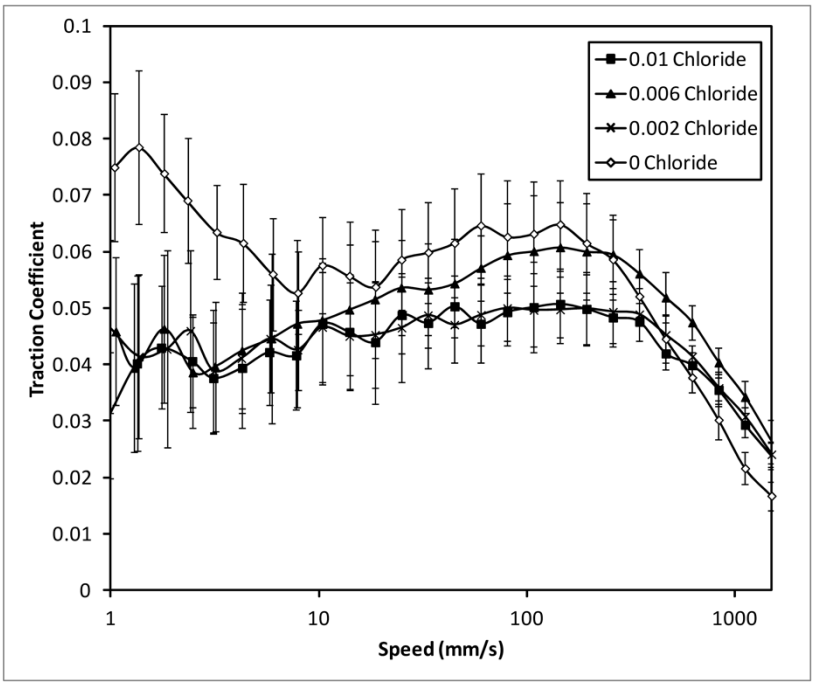
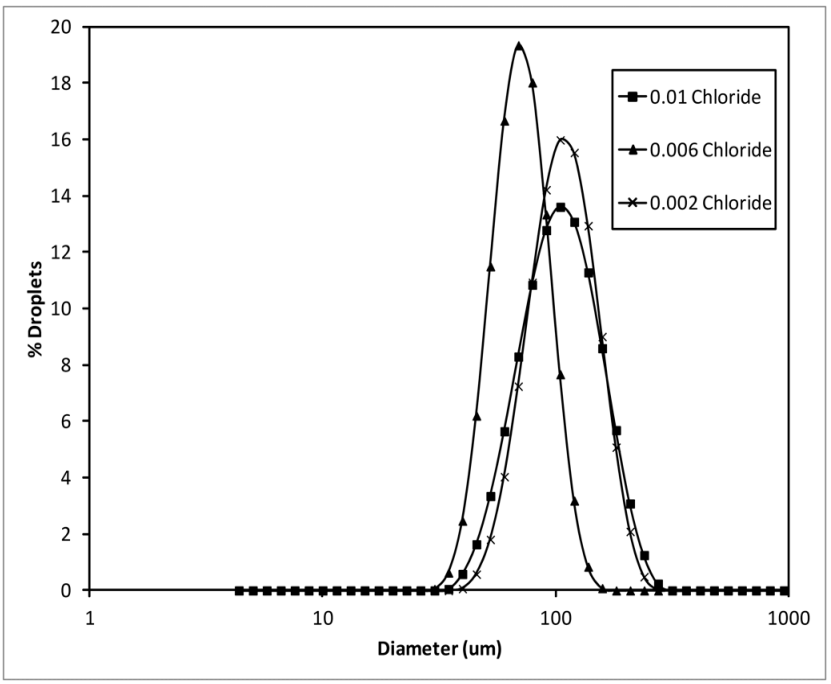


Figure 9. Particle size distributions for agar/chloride systems



Results for thiocyanate lubrication are presented in Figure 10 and follow a similar trend to the chloride in that the friction values for the initial stages of lubrication are again depressed, however the effect is more pronounced (even though particle size distributions are similar, Figure 11). Overall friction is reduced and at the highest concentration a flattening of the curve is more visible, this decrease is suggested to be a result of creating weaker more deformable particles which improve lubrication by entraining more easily (Piculell, et al., 1989).

Figure 10. Stribeck curves for agar/thiocyanate

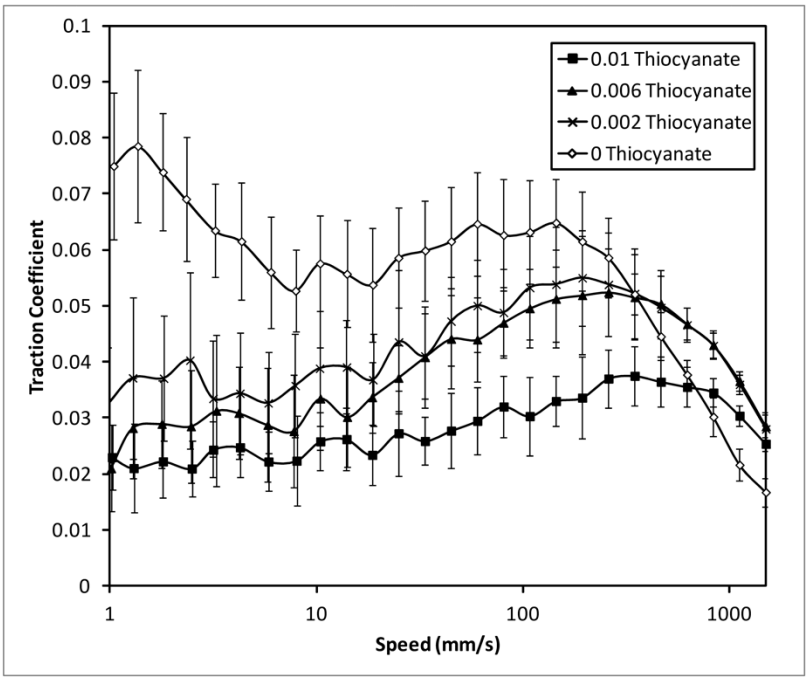
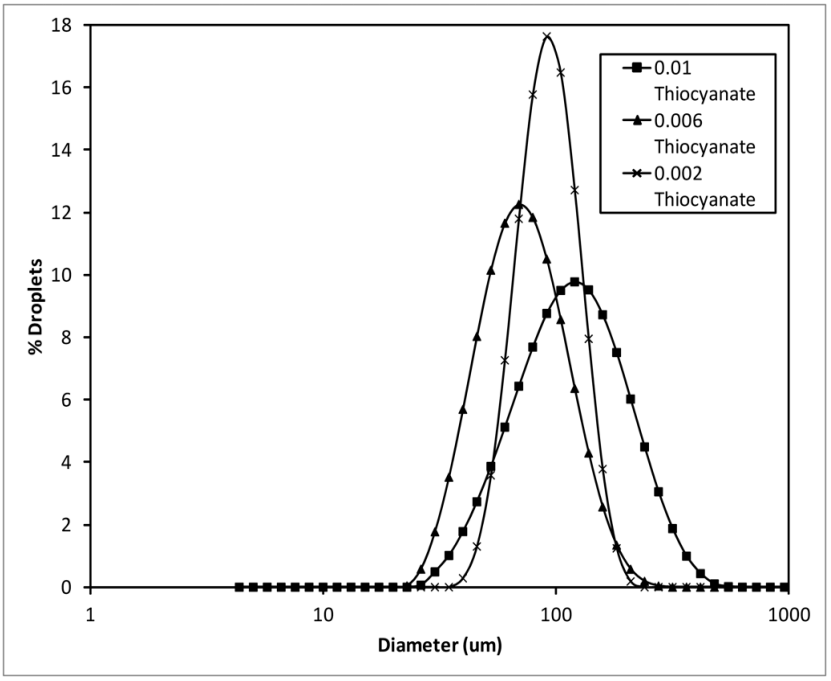


Figure 11. Particle size distributions for agar/thiocyanate systems



At the opposite end of the lyotropic scale, citrate enhances the gelation of the agar raising its gelation temperature and creating harder particles. From Figure 12 it can be seen that an overall increase in friction is observed over pure water/agar gels, with no evidence of two peaks present in Stribeck curves. Again because of the increase in particle sizes and broadening of the peaks this behaviour seems to be hidden. The increases in friction are suggested to be a result of producing larger and possibly more irregular particles cause by the increased gelation speed, the bimodal distribution present in the highest concentration supports this theory (Figure 13).

Figure 12. Stribeck curves for agar/citrate

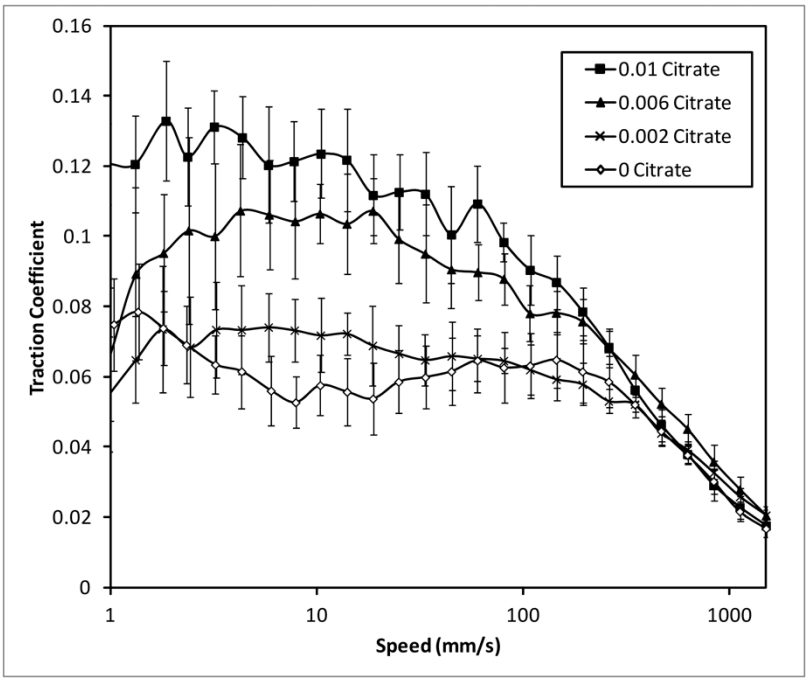
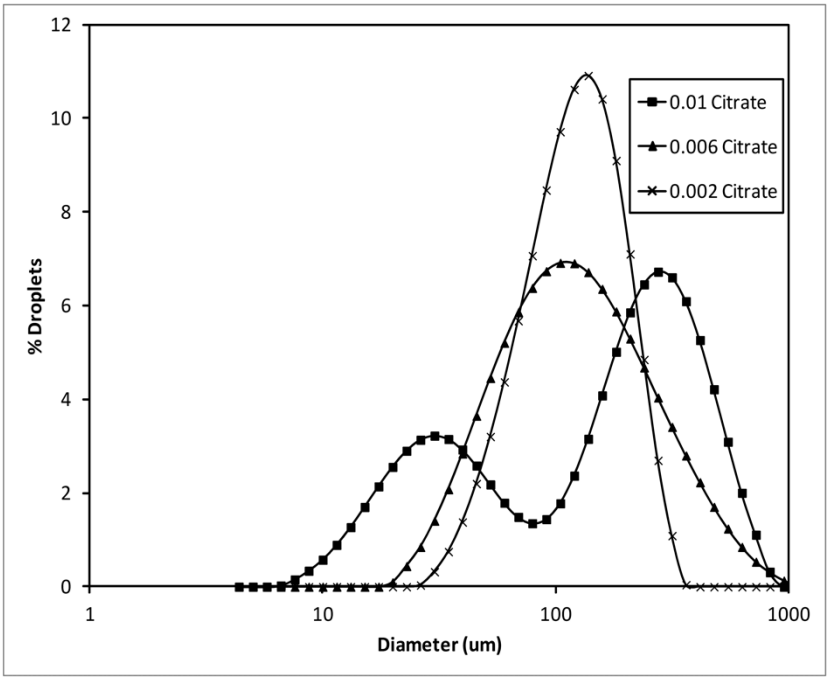


Figure 13. Particle size distributions for agar/citrate systems



Conclusions

Alcohol systems have been shown to reduce friction in the boundary/mixed regime for soft tribology, this effect increases with increasing carbon chain length and builds on earlier hard tribology applications (Jahanmir, 1985). Adding salts with varying anions have also been shown to reduce friction primarily in the boundary regime, this effect follows the lyotropic series with more kosmotropic anions having a larger effect.

Using these solvents as bases for fluid gel production has a marked effect on fluid gel properties and lubrication behaviour. The difference in lubrication behaviour is attributed mainly to the affect on gel properties rather than the contribution of the solvent itself to lubrication. For ethanol a shift in the basic fluid gel lubrication curve is observed to high frictions, and the characteristic double peak remains, suggesting harder and larger particles are formed. When using salts a more significant change is observed in the shape of the lubrication curve removing the double peak. This is primarily a result of larger particle sizes over a greater range being produced. Secondary effects are also observed which shift the level of the Stribeck curve and can flatten its profile as a result of the anions helping or hindering gel formation and therefore its hardness, shape and subsequent entrainment. These effects follow the lyotropic series with anions at each end of the scale having large effects on gel properties and ensuing lubrication behaviour.

These effects are significant for the design and use of fluid gels in complex systems likely to be found in future consumer products and food systems, and as such require further understanding to achieve the desired properties in a finished product.

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